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# Magnetic Nanoparticle Supported Second Generation Hoveyda– Grubbs Catalyst for Metathesis of Unsaturated Fatty Acid Esters

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**Abstract:** The Hoveyda–Grubbs catalyst has been successfully immobilized on surface-modified magnetic nanoparticles with a loading amount of 0.28 mmol ruthenium/g (magnetic support). The supported catalysts were active for the self-metathesis of methyl oleate and macro-monomer in a quantitative

Introduction

The olefin metathesis reaction has been well recognized as a powerful tool to form new C=C bonds in organic compounds.<sup>[1]</sup> The reaction is playing a key role in the new emerging oleochemical industry, which is concerned with producing chemicals from renewable resources such as natural oils and fats. By olefin metathesis, unsaturated fatty acid esters and oils are converted into new products.<sup>[2]</sup> However, before extending the application, it is necessary to recover the metathesis catalysts from the view of both economy and environmental benefit. To date, only a few methods for recovering or separating metathesis catalysts have been investigated, these include chromatographic purification of homogeneous catalysts,<sup>[3]</sup> and aqueous extraction of water-soluble catalysts.<sup>[4]</sup> Despite the great progress achieved so far, the separation and recovery of highly active ruthenium-based homogeneous metathesis catalysts from the product remains a big challenge because these techniques are either difficult to be scaled up or toxic materials are used. Thus, heterogenizing metathesis catalysts has attracted more and more interest, and ruthenium-based metathesis catalysts have been immobilized on various organic and inorganic supports.<sup>[5-7]</sup> The activity of the supported catalyst is highly dependent on the

conversion, respectively. In addition, the catalyst can be easily separated by using a magnet and reused several times with sustained activity.

**Keywords:** fatty acids; immobilization; metathesis; nanoparticles; ruthenium; supported catalysts

nature of the support, however, they all demonstrate improvements in catalyst recovery.<sup>[5–7]</sup>

On the other hand, several reports have been published on metathesis of fatty acid esters.<sup>[2,8]</sup> However, the catalyst recovery issue has not been well addressed till now. To make the processes greener, in general, neat reactions are preferred in fatty acid ester transformations. Consequently, that makes it more difficult to recover the catalyst from a reaction mixture with a high boiling point and high viscosity caused by starting material or products. The conventional purification techniques such as distillation, filtration and chromatography may not be suitable in large-scale operation to separate catalysts and products in the reactions. There is a need to discover a viable process to recover catalysts from these high viscosity product mixtures. Magnetic nanocomposites as catalyst supports have been attracting more and more attention because they can be easily recovered from the reaction mixture simply by using an external magnet.<sup>[9]</sup> In our lab, we are using magnetic nanoparticles as a catalyst support, which can be easily dispersed into a solution homogeneously, to facilitate catalyst recovery of, e.g., a supported palladium catalyst for C-C coupling reactions.<sup>[10]</sup> Herein, we report our preliminary results regarding supported Hoveyda-Grubbs catalyst on magnetic nanoparticles and used in transformation reactions of methyl oleate.

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The catalyst composite can be easily recovered from the reaction mixture by magnet with sustained activity.

# **Results and Discussion**

Carbene-coordinated ruthenium catalysts such as the second generations of Grubbs and Hoveyda-Grubbs catalysts, have demonstrated high activities for olefin metathesis reactions with functional group tolerance.<sup>[1]</sup> Immobilization and activity examinations of these catalysts are necessary for catalyst recovery in green and economically viable industry processes. In our lab, commercially available magnetic nanoparticles with a mean diameter of 100 nm were successfully enriched with ortho-isopropoxystyrene ligands by covalent bonds as shown in Scheme 1. Reaction of the immobilized ligand with second generation Grubbs catalyst produced the supported second generation Hoveyda-Grubbs catalyst. To characterize the supported catalyst 4, we examined it with NMR, IR, XPS, ICP, TGA and TEM technologies. In the <sup>1</sup>H NMR spectra, a broad peak was obtained with a shifted  $\delta$  as compared with normal NMR absorptions. The poor NMR signals may be caused by the magnetic properties of the support material.<sup>[11]</sup> In the near IR spectra [Figure 1 (top)], obvious changes have been found for supported catalyst 4 when compared with free and anchored ortho-isopropoxystyrene ligand 2 and 3, respectively in the range of 2700- $3200 \text{ cm}^{-1}$ . However, in the far IR [Figure 1 (bottom)], 4 and the  $2^{nd}$  generation Grubbs catalyst showed identical peaks in the range of 200-310 cm<sup>-1</sup> for  $v_{Ru-Cl}$  absorptions.<sup>[12]</sup> The results suggest that Ru-Cl bonds in **4** and the 2<sup>nd</sup> generation Grubbs catalyst have similar chemical environments. In addition, 4



Figure 1. Near (top), and far (bottom) IR spectra of related compounds.

also showed obvious absorptions at the frequencies of 108 (broad), 48 and 41 cm<sup>-1</sup>, respectively [Figure 1 (*bottom*)], when compared with the far IR spectrum of the  $2^{nd}$  generation Grubbs catalyst. These absorp-



Scheme 1. Synthesis of magnetic nanoparticle supported Hoveyda–Grubbs catalyst.

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tions may be caused by Ru=C and Ru–O ( $\pi$ -bond) resonances. However, no obvious absorption was found for supported ligand **3** in the far IR spectrum.

In ICP-OES analysis, diluted solutions of the purchased ruthenium atomic absorption standard solution (1000  $\mu$ g/mL) were used to construct the calibration lines. The analytical determinations were performed at the wavelength numbers of 245.657, 267.876 and 349.894 nm, respectively. At these frequencies, elements such as Zr and Cr that could potentially influence our ICP analysis results were not used in our processes.<sup>[13]</sup> The data obtained from the average of the three detection wavelengths were used



Figure 2. TEM image of catalyst 4.

to calculate the Ru concentrations. Samples for ICP analysis were obtained by decomposing the supported catalyst 4 with concentrated HNO<sub>3</sub>. ICP analysis showed that a loading amount of 0.28 mmol Ru/g (magnetic support) was achieved. The modification was also confirmed by TGA results which showed a reduced amount of residues for 3 and 4 compared with the residue from the purchased magnetic support (see Supporting Information Figure S-1). The modification did not cause aggregation of magnetic nanoparticles and the particle size was maintained as observed in TEM after our process. After supporting the ruthenium catalyst, the amount of residue dropped to 53.8 wt% compared with the residues from ortho-isopropoxystyrene ligand enriched magnetic support 3 (62.7 wt%) and the purchased magnetic support (70.3 wt%). These results were consistent with the above ICP analysis. The magnetic nanoparticles loaded with the ruthenium-based second generation of Hoveyda-Grubbs catalyst have also been analyzed with TEM (Figure 2). In the TEM image, only magnetic particle cores with an average of ca. 13 nm have been seen, no other particles are found. Combining all the information, it can be concluded that the ruthenium catalysts have been successfully loaded onto the magnetic support.

The prepared magnetic nanoparticle-supported second generation of Hoveyda–Grubbs catalyst, **4**, has been tested as a catalyst for both self- and cross-meta-thesis reactions. Self-metathesis of methyl oleate, as shown in Scheme 2, was conducted neat at 50 °C with commercially available sources. An isolated yield of 73% with a TOF of 489 h<sup>-1</sup> has been reached after 3 h reaction in a ratio of [methyl oleate]<sub>mol</sub>/[Ru]<sub>mol</sub>=2008. Two products were separated as colorless oils by chromatography. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds are consistent with literature values and con-



Scheme 2. Metathesis reactions of methyl oleate and macro-monomer.

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firmed them as 9-octadecene and the second product as dimethyl 9-octadecene-1,18-dioate, respectively.[8a] The activity is slightly lower than that of the second generation of Grubbs catalyst which exhibited TOFs of  $652 h^{-1}$  at  $40 \degree C^{[8d]}$  and  $700 h^{-1}$  at  $50 \degree C^{[2a]}$ , respectively. It should be pointed out that our catalyst could be easily separated from the reaction mixture by attraction of a magnet. The magnetic-supported catalysts were attracted onto the inner surface of the reactor, a round-bottom flask by using an external magnet (1.14 T) when the reaction mixture was kept in a stationary condition. The product mixture could be collected easily by decantation, and the attracted catalysts were further reused after washing with dichloromethane to remove any absorbed starting material or product. The concentrations of leaching Ru in the product mixture combined with the wash solution obtained from above reactions are less than 3.0 ppm based on ICP results. In addition, after 3 runs, no significant aggregation and size changes of the magnetic nanoparticle support were observed as confirmed by TEM images. It is very important to note that our catalyst 4 could be recycled easily and reused at least 5 times under our conditions with TOFs of  $488 h^{-1}$ ,  $484 h^{-1}$ ,  $487 h^{-1}$ ,  $485 h^{-1}$ ,  $486 h^{-1}$ , respectively. Since our reactions were performed neat, the approach avoids solvent waste, and thus is beneficial in terms of green chemistry. These results demonstrate a significant improvement of the existing catalyst recycling procedures and the process is more viable for the use of renewable materials. To confirm that the high activity was contributed by the supported ruthenium catalyst, contrast experiments have been investigated under the same conditions in a dichloromethane solution obtained from the wash solution of catalyst. No isolable products were found after similar purification. The results confirmed that the supported Hoveyda-Grubbs catalyst provides the high activity rather than a leaching catalyst species. At present, although the classic metathesis mechanism might be applicable to catalyst 4, a further confirmation study is undergoing in our lab using on-line IR technology.

To investigate the catalytic activity of **4** to a functional polymer, macro-monomer, 9-decen-1-ol tailed poly(D/L-lactide), was synthesized (Scheme 2). A colorless polymer with an MW of  $1.75 \times 10^4$  (PDI=1.73) was produced with SnOct<sub>2</sub> as catalyst. As shown in Scheme 2, the macro-monomer underwent self-metathesis in a mixed solvent of dichloromethane and *N*,*N*-dimethylacetamide, with a ratio of [macro-monomer]<sub>mol</sub>/[Ru]<sub>mol</sub>=98, a new product with double molecular weight (Mw= $3.56 \times 10^4$ , PDI=1.74) was formed based on gel permeation chromatography analysis as expected. In the self-metathesis reaction, **4** exhibited a TOF of 29 h<sup>-1</sup>. In contrast, under the same conditions, the 2<sup>nd</sup> generation Grubbs catalyst was more active than **4**, a higher TOF of 43 h<sup>-1</sup> was achieved in a ratio of  $[macro-monomer]_{mol}/[2^{nd} generation Grubbs catalyst]_{mol} = 156.$ 

Cross-metathesis of unsaturated fatty acid esters such as methyl oleate, with a normal olefin is an elegant method with great potential synthetic value for generating the desired unsaturated alkenes.<sup>[2]</sup> However, more consideration should be taken for catalyst selection. A more desirable catalyst should be able to tolerate a wide range of functional groups such as ester groups, and exhibit significant selectivity for cross-metathesis rather than self-metathesis of olefins. As a model reaction, we investigated the cross-metathesis of methyl oleate with methyl acrylate. A procedure similar to the literature report was performed in bulk with conditions of [methyl oleate]<sub>mol</sub>/[Ru]<sub>mol</sub>= 497, [methyl acrylate]<sub>mol</sub>/[methyl oleate]<sub>mol</sub> = 10 in neat conditions.<sup>[8f]</sup> After purification with thin layer chromatograph (TLC), 1-methylundec-2-enoate and 1,11-dimethylundec-2-enedioate (based on NMR spectra compared with literature data<sup>[8f]</sup>) were obtained as the major products. An isolated yield of 60% with a TON of 300 (TOF =  $12 \text{ h}^{-1}$ ) has been achieved after 25 h at 45 °C. Similar to the self-metathesis reaction of methyl oleate, the catalyst could be recovered by magnetic attraction, and reused for at least 3 times with slightly reduced TOFs of  $11.8 \text{ h}^{-1}$ ,  $11.9 \text{ h}^{-1}$ ,  $11.8 \text{ h}^{-1}$ , respectively. These activities are much higher than the 2<sup>nd</sup> generation Grubbs catalyst (TOF <1 h<sup>-1</sup>), and comparable with unsupported 2<sup>nd</sup> generation Hoveyda–Grubbs catalyst  $(TOF = 11 h^{-1})$ .<sup>[8f]</sup> The concentrations of leaching Ru in the product mixture combined with the wash solution obtained from above reactions are very small, less than 4.0 ppm (based on ICP analysis).

# Conclusions

In conclusion, we have successfully immobilized the second generation Hoveyda–Grubbs catalyst on magnetic nanoparticles by forming covalent bonds and demonstrated that the magnetic nanocomposites are high effective for both self- and cross-metathesis reactions of methyl oleate. The supported catalysts could be well dispersed in the organic reaction mixture to produce a false homogeneous catalyst system. In addition, the unique catalyst could be easily separated by magnetic attraction with sustained activity.

# **Experimental Section**

#### **General Remarks**

All operations were conducted under an argon atmosphere with in a glove box or standard Schlenk lines. Magnetic support ( $50 \text{ mgmL}^{-1}$ , 100 nm, matrix with starch) was provided

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by chemicell GmbH. Ruthenium atomic absorption standard solution (1000 µg/mL, Ru in 5% HCl) and other reagents were supplied from Sigma-Aldrich Pte. Ltd. Compound 1 was prepared according to the literature.<sup>[5a] 1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker Fourier-Transform multinuclear spectrometer at 400 and 100.6 MHz, relative to external Me<sub>4</sub>Si (TMS) standard. Near infrared (IR) spectra were measured using a BIO-RAD spectrophotometer with the KBr pellet technique. Far infrared spectra were measured using a Bruker FT-IR, Vertex 70 spectrophotometer with neat sample pellets. ICP analysis was determined with a VISTA-MPX, CCD Simultaneous ICP-OES analyzer. The TGA analyses were carried out on an SDT 2960 Simultaneous DSC-TGA analyzer. Transmission electron microscopy (TEM) measurements were carried out on a JEOL Tecnai-G<sup>2</sup>, FEI analyzer at 200 kV. The MS was measured on a Thermo Finnigan MAT XP95 analyzer using the EI mode. Molecular weights and molecular weight distributions of the polymers were determined by means of gel-permeation chromatography (GPC: Agilent GPC), using dichloromethane as eluent with a column set of 2xPLgel 5 µm MIXED-C. The weight average molecular weight and polydispersity index ( $M_w$  and  $M_w/M_n$ , respectively) were calculated on the basis of polystyrene standards. Flow rate =  $1.0 \text{ mLmin}^{-1}$ , injected volume =  $50 \,\mu$ L.

#### Synthesis of Compound 2

NaH (0.288 g, 0.012 mol) was added carefully to a solution of  $\mathbf{1}^{[5a]}$  (1.780 g, 0.01 mol) in dry tetrahydrofuran (15 mL) in a glove box. After stirring for 3 h at room temperature, sodium bromoacetate (1.642 g, 0.01 mol) was added to the reaction mixture and the mixture was refluxed overnight. The solvent was removed under vacuum, and distilled water (7 mL) was added to the residue. Extraction was carried out with 10 mL of diethyl ether to remove unreacted starting material. After acidification of the aqueous layer with 1N HCl, the reaction mixture was extracted with diethyl ether  $(3 \times 100 \text{ mL})$ , the combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum followed by purification with chromatography (SiO<sub>2</sub>, eluted with a mixted solvent of hexane/diethyl, v/v=5/1) ether to give pure product 2; yield: 2.056 g (87%). Elemental analysis for calcd. 2 C13H16O4 (%): C 66.09, H 6.83; found: C 65.87, H 6.94; EI-MS: m/z = 233.81 (M<sup>+</sup>-2H), 234.82 (M<sup>+</sup>-H); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.32$  (d, 6H, 2CH<sub>3</sub>), 4.42 (m, 1H, CHO), 4.65 (s, 2H, OCH<sub>2</sub>CO<sub>2</sub>), 5.25 (d, 1H, =CH<sub>2</sub>), 5.72 (d, 1H, = $CH_2$ ), 6.77–7.08 (m, 4H, C<sub>6</sub> $H_3$ , CH=CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 21.94$  (2 C, 2CH<sub>3</sub>), 65.43 (1 C, CHMe<sub>2</sub>), 72.16 (1C, OCH<sub>2</sub>CO<sub>2</sub>), 112.47, 114.45, 114.63, 116.34, 129.25, 131.25, 150.19, 151.44 (8C, C<sub>6</sub>H<sub>3</sub>, CH=CH<sub>2</sub>), 173.55 (1C,  $CO_2$ ). IR (KBr, pellet): v = 2976 (s, s), 2933 (s, s), 1735 (s, s), 1588 (m, m), 1491 (s, s), 1432 (m, s), 1374 (m, s), 1286 (m, s), 1209 (s, br), 1137 (m, s), 1110 (s, s), 1078 (m, s), 956 (m, s), 921 (m, s), 873 (m, s), 854 (m, s), 807 (m, s), 772 (w, s), 676 (w, s), 504 cm<sup>-1</sup> (w, s).

#### Synthesis of Compound 3

Commercially available magnetic support (0.100 g) was suspended in a mixture of dichloromethane (20 mL) and *N*,*N*-dimethylacetamide (DMA) (5 mL). Compound **2** (0.30 g, 1.27 mmol), 4-dimethylaminopyridine (DMAP) (0.134 g,

1.1 mmol) and dicyclohexylcarbodiimide (DCC) (0.288 g, 1.40 mmol) were added to the above solution with vigorous stirring at 0°C. After addition, the resulting mixture was stirred at room temperature for 6 h. An external magnet was used to recover the magnetic nanocomposite from the reaction mixture. The separated nanocomposite was washed with dimethyl sulfoxide ( $2 \times 50$  mL), dichloromethane ( $2 \times 10$  mL) followed by deionized water ( $2 \times 10$  mL) and dried under vacuum at 50°C for 3 days to produce the ligand-supported magnetic nanoparticles (yield: 0.178 g) with a ligand loading of 0.33 mmolg<sup>-1</sup>(based on elemental analysis). The obtained sample was also analyzed by IR, and TGA.

#### Synthesis of Compound 4

A literature method was used to immobilize the ruthenium catalyst.<sup>[14]</sup> Grubbs second generation catalyst (0.43 g, 0.506 mmol) and CuCl (0.05 g, 0.505 mmol) were added to a solution of **3** (0.1 g) in a mixed solvent of dichloromethane (25 mL) and DMA (10 mL) and furthered reacted at 40 °C for 3 h. External magnets were used to separate the magnetic nanocomposite from the reaction mixture. The separated nanocomposite was then washed with dichloromethane (2× 10 mL) dimethyl sulfoxide (2×10 mL) and acetone (2× 15 mL) followed by drying under vacuum to produce a brown product with an Ru loading of 0.28 mmolg<sup>-1</sup> (based on ICP analysis). The product was also subjected to analysis with TGA, TEM and IR, respectively.

#### Synthesis of Macro-monomer

Macro-monomer was prepared according to the literature report.<sup>[15]</sup> D/L-Lactide (2.89 g, 20 mmol), 9-decen-1-ol (0.016 g, 0.1 mmol) and SnOct<sub>2</sub> (0.083 g, 0.2 mmol) were dissolved in 70 mL toluene. The resulting solution was refluxed for 6 h before cooling to room temperature. All solvents were removed under reduced pressured. The obtained residue was then re-dissolved in a small amount of  $CH_2Cl_2$  and precipitated with cold methanol. The resulting solid was collected by filtration and washed with  $2 \times 20$  mL cold methanol followed by drying at 50 °C under vacuum for 2 days to give the solid product; yield: 2.30 g (MW= $1.75 \times 10^4$ , DPI=1.73 based on GPC analysis). The product was also subjected to analysis with IR.

#### Self-Metathesis of Methyl Oleate using 4 as Catalyst

A literature procedure was used to conduct the self-metathesis of methyl oleate.<sup>[8c]</sup> Methyl oleate (4.50 g, 15.18 mmol) was added to a dry round-bottom flask equipped with a magnetic stirring bar. Compound **4** (27.0 mg, 7.56 µmol [Ru]) ([methyl oleate]<sub>mol</sub>/[Ru]<sub>mol</sub>=2008) was added with vigorous stirring. The resulting mixture was heated to 50 °C for 3 h before cooling to room temperature and the catalyst was recovered with an external magnet. The recovered catalyst was washed with dry dichloromethane and dried under vacuum for a subsequent run. The resulting mixture was purified with flash chromatography (SiO<sub>2</sub>, eluted with hexane/diethyl ether, v/v=10/1) to produce 9octadecene (yield: 2.76 g) and dimethyl 9-octadecene-1,18dioate (yield: 3.75 g) with an isolated yield of 73% (TOF= 489 h<sup>-1</sup>). **9-Octadecene:** <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.89$  (t, 6H, 2*CH*<sub>3</sub>), 1.29–1.33 (br. m, 24H, 12*CH*<sub>2</sub>), 1.97–2.02 (m, 4H, 2 *CH*<sub>2</sub>CH=), 5.40–5.42 (m, 2H,*CH*=*CH*); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.12$  (2*C*, 2*CH*<sub>3</sub>-), 22.69 (2*C*, 2*CH*<sub>2</sub>CH<sub>3</sub>), 29.17, 29.32, 29.50, 29.66, 31.91, 32.61 (12*C*, 12*CH*<sub>2</sub>), 130.36 (2*C*, 2*C*H=).

**Dimethyl 9-octadecene-1,18-dioate:** <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ =1.28–1.29 (br. m, 16H,8CH<sub>2</sub>), 1.59–1.63 (br. t, 4H, 2CH<sub>2</sub>), 1.95–1.96 (br. m, 4H, 2CH<sub>2</sub>), 2.30 (t, 4H, 2CH<sub>2</sub>), 3.67 (s, 6H, 2CO<sub>2</sub>CH<sub>3</sub>), 5.36–5.38 (m, 2H, CH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ =24.95, 28.94, 29.11, 32.55, 34.11 (12 C, 12 CH<sub>2</sub>), 51.45 (2 C, 2 CH<sub>2</sub>CO<sub>2</sub>), 130.32 (2 C, 2 CH=), 174.36 (2 C, 2 CO<sub>2</sub>); EI-MS: *m/z*=363.25 (M<sup>+</sup>+Na<sup>+</sup>).

#### Self-Metathesis of Macro-monomer using 4 as Catalyst

A similar procedure to the self-metathesis of methyl oleate was used to conduct the self-metathesis of macro-monomer. From 1.2 g (68.6 µmol, based on MW) of the above prepared macro-monomer, with **4** (2.5 mg, 0.70 µmol) ([macro-monomer]<sub>mol</sub>/[Ru]<sub>mol</sub>=98) in a mixture of (DMA) (5 mL) and dichloromethane (10 mL) the polymer was obtained after precipitation with cold methanol from dichloromethane and drying in vacuum at 50 °C for 2 days; isolated yield: 1.10 g (90%, TOF=29 h<sup>-1</sup>).

The procedure above was also conducted with second generation Grubbs catalyst. From 1.2 g (68.6 µmol, based on MW) of the above prepared macro-monomer, with second generation Grubbs catalyst (0.37 mg, 0.44 µmol) ([macro-monomer]<sub>mol</sub>/[2<sup>nd</sup> generation Grubbs catalyst]<sub>mol</sub>=156), the polymer was obtained after drying; isolated yield: 1.0 g (82%; TOF=43 h<sup>-1</sup>). The product was subjected to analysis with NMR, IR and GPC (MW=3.56×10<sup>4</sup>, DPI=1.74). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ =16.65 (1C, CH<sub>3</sub>), 69.01 (1C, CHO), 169.62 (1C, CO<sub>2</sub>); IR (KBr pellet): v=3651(w, s), 3560 (w, s), 3510 (w, s), 2998 (m, s), 2947 (m, s), 2087 (vw, br), 1760 (vs, s, v<sub>CO</sub>), 1457 (s, s), 1386 (s, s), 1361 (s, s), 1213 (vs, s), 1186 (vs, s), 1134 (vs, s), 1093 (vs, s), 1045 (s, s), 957 (w, s), 921 (w, s), 872 (m, s), 756 (m, s), 694 (m, s), 507 cm<sup>-1</sup> (w, s).

#### Cross-Metathesis of Methyl Oleate with Methyl Acrylate using 4 as Catalyst

A literature method was used to perform the reaction.<sup>[8f]</sup> Catalyst **4** (115 mg, 32.2 µmol,) was added to a mixture of methyl acrylate (14.0 g, 0.16 mol,) and methyl oleate (4.74 g, 16 mmol) ([methyl oleate]<sub>mol</sub>/[Ru]<sub>mol</sub>=497) with continuous stirring for 10 min. The reaction mixture was stirred magnetically at 45 °C for 25 h. The excess of methyl acrylate was evaporated under vacuum and the residue was purified by TLC developed with hexane/diethyl ether (v/v=4/1) to produce methyl undec-2-enoate (yield: 1.90 g) and dimethyl undec-2-ene-1,11-dioate (yield: 2.32 g), respectively in an isolated yield of 60% (TOF=12 h<sup>-1</sup>).

**Methyl undec-2-enoate:** <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.88$  (t, 3H, CH<sub>3</sub>), 1.27–1.28 (br, 10H, 5CH<sub>2</sub>), 1.43–1.47 (m, 2H, CH<sub>2</sub>), 2.17–2.22 (dt, 2H, CH<sub>2</sub>C=), 3.72 (s, 3H, OCH<sub>3</sub>), 5.80– 5.84 (d, 1H, =CHCO<sub>2</sub>), 6.94–7.01 (m, 1H, CH<sub>2</sub>CH=C); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.05$ , 22.62, 27.99, 29.11, 29.17, 29.32, 31.81, 32.20 (7 C, 7 CH<sub>2</sub>), 51.31 (1 C, CH<sub>3</sub>CO<sub>2</sub>), 120.77, 149.80 (2 C, CH<sub>2</sub>CH=CHCO<sub>2</sub>), 167.16 (1 C, CO<sub>2</sub>): EI-MS: m/z = 221.15 (M<sup>+</sup>+Na<sup>+</sup>).

**Dimethyl undec-2-ene-1,11-dioate:**<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.31 (br. s, 6H, 3 *CH*<sub>2</sub>), 1.45 (br. s, 2H, *CH*<sub>2</sub>), 1.62 (br. s, 2H, *CH*<sub>2</sub>), 2.17–2.22 (dt, 2H, *CH*<sub>2</sub>), 2.28–2.32 (t, 2H, *CH*<sub>2</sub>CO<sub>2</sub>), 3.67 (s, 3H, CO<sub>2</sub>*CH*<sub>3</sub>), 3.72 (s, 3H, CO<sub>2</sub>*CH*<sub>3</sub>), 5.80–5.83 (d,1H, =*CHCO*<sub>2</sub>), 6.93–6.70 (m, 1H, *CH*=*CHCO*<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 24.89, 27.95, 28.92, 29.01, 32.17, 34.04 (7C, 7*CH*<sub>2</sub>, one signal is overlapped), 51.37 (2C, 2CO<sub>2</sub>*CH*<sub>3</sub>), 120.91, 149.65 (2C, *CH*=*CH*), 167.15, 174.22 (2C, 2*CO*<sub>2</sub>); EI-MS: *m/z* = 265.15 (M<sup>+</sup>+Na<sup>+</sup>).

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